

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
1 August 2002 (01.08.2002)

PCT

(10) International Publication Number  
**WO 02/059388 A1**

(51) International Patent Classification<sup>7</sup>: **C22C 33/02**

(21) International Application Number: **PCT/GB02/00176**

(22) International Filing Date: 17 January 2002 (17.01.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
0101770.6 24 January 2001 (24.01.2001) GB  
0120401.5 22 August 2001 (22.08.2001) GB

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(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Declaration under Rule 4.17:**

— of inventorship (Rule 4.17(iv)) for US only

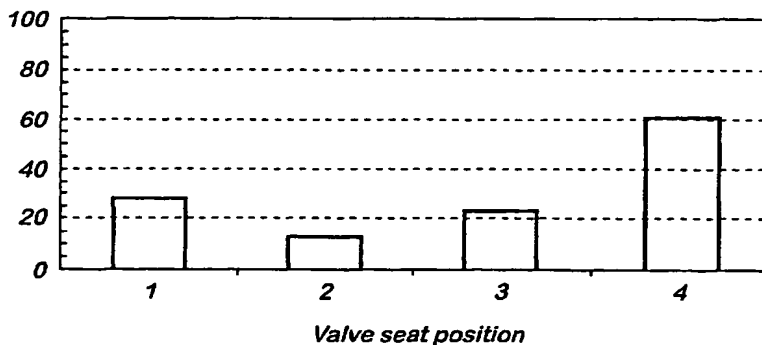
**Published:**

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **SINTERED FERROUS MATERIAL CONTAINING COPPER**

Exhaust vsi wear,  $\mu\text{m}$



(57) Abstract: A process for the manufacture of a ferrous-based sintered article containing copper in the range from 12 to 26 weight% is described, the process including the steps of: making a powder mixture having a desired composition, at least a proportion of a total content of iron and copper being provided by an iron powder having copper indivisibly associated therewith for instance being pre-alloyed or diffusion bonded; compacting said powder mixture to form a green compact of an article to be produced and sintering said green compact.

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## SINTERED FERROUS MATERIAL CONTAINING COPPER

- 5 The present invention relates to sintered ferrous materials, articles made therefrom and to a method for their manufacture particularly, ferrous materials containing copper.
- 10 The powder metallurgy route enables the design of metallic materials which it is not possible to make by conventional casting and ingot working processes. It is known to infiltrate sintered ferrous powder metallurgical products with metals having lower melting points such as
- 15 lead and copper, for example. Lead is used to improve machinability of sintered ferrous materials whilst copper also has this effect but also has other desirable properties which it confers on the sintered material. Lead is nowadays avoided due to its harmful environmental
- 20 properties. Copper improves machinability and also improves the thermal conductivity of the sintered article.
- 25 Copper infiltrated products are used extensively in the automotive industry for applications such as valve seat inserts in the cylinder heads of internal combustion engines, for example. Such products have to perform under very arduous conditions including repeated impact loading, marginal lubrication, elevated service
- 30 temperatures and hot corrosive gases. Properties to withstand these conditions are achieved by the suitable design of the ferrous matrix system. Such ferrous matrices are often highly alloyed which adversely affects machinability. Machinability is important to an engine

builder in a production context as it affects productivity. Copper infiltration provides improved machinability whilst the copper itself provides improved thermal conductivity which has the effect of lowering  
5 operating service temperatures which helps to retain mechanical properties.

The infiltration process is effected by stacking a copper alloy compact in contact with the ferrous component and  
10 passing the stacked assembly of the two items through a sintering furnace at a sintering temperature in the region of about 1100°C under an inert or reducing gaseous atmosphere thus effecting sintering and infiltration simultaneously. During this sintering process the copper  
15 alloy compact melts and the molten alloy infiltrates and fills the pores of the ferrous component by capillary action. Only interconnected pores can be filled in this manner, isolated or otherwise unconnected porosity cannot be so filled. The composition of the copper alloy compact  
20 is so chosen that it is compatible with the ferrous material and undesirable reactions or erosion thereof is avoided as far as possible. The weight of the copper alloy compact is chosen so as to be able to fill the majority of the pores, however, as noted above there is  
25 inevitably some residual porosity.

In a variation of the above process, the copper alloy compact is stacked with a pre-sintered ferrous component and the two passed through a sintering furnace to effect  
30 infiltration.

The infiltration process is an expensive process owing to the extra process steps involved. The process requires the additional steps of: making a separate copper alloy

powder mixture; pressing suitable compacts of the correct weight from the powder mixture; stacking the compacts with the ferrous articles themselves prior to passing through the sintering furnace; and, barrelling the  
5 sintered and infiltrated articles after cooling to remove the powdery deposit which inevitably forms on the articles during the sintering process.

10 In conventional copper infiltrated ferrous products, the level of copper content generally lies in the range from 15 to 25 weight%. In non-infiltrated products it is common to add up to about 5 weight% of copper powder in the pre-compacted powder mixture. Such relatively small  
15 additions of copper to non-infiltrated ferrous materials assist the sintering process due to the liquid copper phase being present.

20 People have tried to add levels of copper achieved in the infiltration process by means of additions of the appropriate amount of elemental copper in the initial powder mixtures prior to compaction and sintering. However, due to differences in, for example, powder  
25 particle size, powder density and powder particle morphology, segregation of the copper tends to occur during handling of the powder mixtures. Such powder segregation causes unacceptable variations in the  
30 resulting products. Where only small amounts of elemental copper powder is present such as the case of up to about 5 weight% noted above, segregation still occurs but the effect in the resulting products is minimised and does not cause a serious problem.

At one time components such as valve seat inserts for engines having the most arduous service environment were

made entirely from highly alloyed steels such as M3/2 class steels for example. Such steels contain relatively high quantities of chromium, tungsten, molybdenum, vanadium and the like. Whilst components made from such materials have excellent performance and long service lives, they are inherently expensive to make and process. They are expensive to make firstly because of the high intrinsic material cost and secondly expensive to process because of the difficulty in machining components having high contents of hard carbide in the microstructure thereof. In the never ending quest to lower costs, much work has been carried out to reduce material cost by adding relatively high proportions of substantially pure iron powder to the powder mixes and consequently reducing processing costs by making the resulting sintered materials easier to machine by reducing the amount of hard phases and adding phases which assist machinability such as copper or chip-breaking phases.

A disadvantage in terms of performance and longevity of life of these newer materials such as may be exemplified in GB-A-2 188 062 for example is the retention in the cores of the iron grains, formed by the sintering together of the original compacted iron powder particles in the powder mixture, of soft ferrite phase which can deleteriously affect the wear and strength properties thereof. Such materials may initially comprise mixtures of about 50% of the highly alloyed M3/2 material, for example, and about 50% of pure iron powder and minor additions of carbon, die lubricating waxes and the like. Even when fully sintered the iron grains have ferrite cores with only some diffusion of chromium, from the M3/2 regions, into the surface regions of the iron grains, where martensite may be formed, after sintering. This

structure still applies even when the material is infiltrated or when up to about 5 weight% of elemental copper has been added to the powder mixture.

5 It is an object of the present invention to provide a process for making ferrous material articles having a high copper content commensurate with that of infiltrated material but without the disadvantage of the additional process steps required in the prior art processes.

10

Other advantages will become apparent from the description of the invention below.

15 According to a first aspect of the present invention, there is provided a process for the manufacture of a ferrous-based sintered article containing copper in the range from 12 to 26 weight%, the process including the steps of: making a powder mixture having a desired composition, at least a proportion of a total content of  
20 iron and copper being provided by an iron powder having copper indivisibly associated therewith; compacting said powder mixture to form a green compact of an article to be produced and sintering said green compact.

25 The copper content is primarily intended to enhance the thermal conductivity of articles produced, however, other important benefits are also provided to articles made by the method of the present invention. Below 12 weight% copper the required enhancement in thermal conductivity  
30 is not achieved whilst above 26 weight% "bleeding" of molten copper from the material during sintering is a problem.

Preferably, the copper content may lie in the range from 15 to 20 weight%.

5 In the process according to the present invention, the iron powder indivisibly associated with copper is effectively a pre-alloyed powder in that the individual powder particles comprise both iron and copper and consequently significant segregation between the iron and copper is not possible. The iron and copper powder  
10 particles may be selected from two basic types of powder stock: a pre-alloyed iron-copper powder; or, a diffusion bonded iron-copper powder. The pre-alloyed iron-copper powder may be produced by known techniques of melting the constituent materials together and then atomising the  
15 molten melt by water or gas, for example, to produce the required pre-alloyed powder. The diffusion bonded iron-copper material is produced by making a mixture of elemental iron and copper powders, for example, and passing the mixture, uncompacted, through a furnace such  
20 that diffusion between the particles occurs so as to bond them together. The "cake" so formed is given a light crushing operation to break it up into particles comprising both iron and copper adhered to each other. Such a process causes diffusion of some copper into the  
25 outer regions of each iron particle.

The method of the present invention obviates several of the process steps of prior art processes in that a separate copper alloy powder mixture and consequent  
30 compacts do not need to be made, they do not need to be stacked with the ferrous material compacts and the final sintered articles do not need to be treated to remove the adherent deposit thereon as with prior art infiltration processes.

A particular advantage conferred by the method of the present invention relates to the processing of those ferrous materials which comprise mixtures of an alloyed steel powder and a low-alloy iron or substantially pure iron powder. It is known to use such mixtures with additions of carbon powder, for example, and to process them by compaction, sintering and post-sintering thermal treatment into articles such as valve seat inserts for internal combustion engines, for example. Such prior art materials may or may not be infiltrated with a copper alloy by one of the conventional processes described above. Such materials are exemplified by those materials and production processes described in GB-A-2 188 062 and EP-A-0 312 161, for example. These materials may comprise a proportion, e.g. about 50 weight% of a highly alloyed steel powder with about 50 weight% of a substantially pure iron powder. The alloyed steel powder usually contains chromium which under the prevailing sintering conditions of about 1100°C is one of the most mobile element atoms after carbon, in terms of rate of diffusion, of those alloying elements which promote the formation of martensite on cooling of the article following sintering. Carbon atoms are the most mobile, moving into the interstices of the iron atoms in the crystal structure. However, since chromium is of a similar atomic size and weight to iron it substitutes for iron and consequently has a similar mobility to iron under the prevailing sintering conditions. The presence of chromium promotes the formation of martensite in those regions of the sintered material into which it diffuses, the martensite being formed on cooling of the material at the end of the sintering cycle. Sintering is frequently effected for such articles in furnaces which have



continuous moving means, such as a belt or a walking-beam type mechanism, for transporting the articles, generally supported on trays for example, through the furnace. Generally, a first portion of the furnace raises the temperature of the articles to the sintering temperature; a second portion maintains the articles at the sintering temperature; and, a third portion allows the articles to cool from the sintering temperature to a temperature which will preclude significant oxidation of the articles on exit from the sintering furnace. The articles are generally sintered under a continuous protective gas atmosphere flowing through the furnace which serves to provide either a neutral or reducing atmosphere and preclude air (oxygen) from entering the furnace. The atmosphere is at substantially atmospheric pressure with only a slight positive pressure within the furnace to prevent air from entering therein. Where the sintered material contains a significant quantity of iron powder in the original mix it is frequently found that the iron grains resulting from the sintering of the compacted iron powder particles possess a microstructure ranging from ferrite to pearlite and mixtures of the two phases, depending upon the carbon content, in the core of the iron-rich non-tool steel regions. The outer region of the iron grains generally comprises martensite resulting from chromium which has diffused in during the sintering operation but the core remains essentially as ferrite or pearlite or a mixture of ferrite and pearlite depending upon the added carbon level. In the as-sintered condition, the iron-rich non-tool steel phase or grain structure consists of mainly pearlite, though there may be some ferrite, at the centre and the outer regions of the grains are a mixture of martensite/bainite. If there is any retained austenite in the sintered article it is

generally transformed by cryogenic treatment after sintering. During a tempering operation usually carried out after cryogenic treatment, partial decomposition of the pearlite phase occurs leading to the formation of ferrite areas within the iron-rich grains or phase. This can result in the material having inferior wear properties due to the presence of ferrite and also lower strength due to the ferrite. The post-sintering thermal treatments comprising cryogenic treatment to transform any remaining  $\gamma$ -phase (austenite) to martensite followed by tempering treatments are to reduce the degree of hardness and brittleness of the martensite phase rather than to effect decomposition of the pearlite which is an undesirable side effect of the tempering process. Since the tempering treatment is carried out at a temperature in excess of the expected service temperature, size stability of the article in its service environment (e.g. a valve seat insert in the combustion chamber of an internal combustion engine) is ensured. However, such treatments do not affect the presence (other than to be responsible for generating at least a proportion of the ferrite) of the ferrite phase or its inherently poor wear and mechanical properties.

It has been found that with the method of the present invention that there appears to be a synergistic effect of the copper (either from the diffusion-bonded form or in the pre-alloyed form with the iron) and chromium together in promoting the diffusion of copper and chromium towards the centre of the iron grains and, instead of the core of the iron grains remaining as ferrite or pearlite or a mixture of these, the core of the iron grains is found to transform to martensite during normal furnace cooling. Sintered ferrous materials

made according to the process of the present invention using either pre-alloyed iron-copper or diffusion bonded iron-copper powders reveal the presence of martensite in the cores of the iron-rich grains due to the diffusion of chromium or other martensite promoting elements into the iron grains. The martensite is formed during the cooling of austenite and any retained austenite is transformed by cryogenic treatment following sintering. During the cooling process from the sintering temperature some of the austenite can also transform to bainite. The martensite may then be tempered to form a structure of tempered martensite which is readily machinable. However, it is important to note that the previously soft ferritic/pearlitic cores of the iron grains now comprise material which is harder, stronger and more wear resistant due to the process of the present invention. It is believed that the processing used to form the pre-alloyed and diffusion bonded iron-copper material causes at least some diffusion of the copper phase into the iron constituent and the presence of the copper assists in the diffusion of chromium and other martensite promoting elements into the cores of the iron grains formed on sintering thus, enabling martensite to be formed.

Tests making materials according to the method of the present invention and making substantially identical materials by prior art infiltration processes, but using substantially identical processing parameters of pressing pressure and sintering temperature for example, have shown the beneficial effects of using an iron-copper pre-alloy or diffusion bonded powder as described hereinabove. Materials of largely identical composition except for the copper content were made by 1) the method of the present invention; 2) by the route of simultaneous

sintering and infiltration; and, 3) by adding 13 weight% elemental copper powder to the initial powder mixture and sintering (i.e. without infiltration and without the addition of pre-alloyed iron-copper powder).

5

Materials made by conventional infiltration techniques under the same processing conditions do not show the beneficial effect of martensite formation in the iron grain core. Analysis by scanning electron microscope has shown the presence of chromium in the particle core in materials made by the method of the present invention. It is to be emphasised that the processing conditions used in the comparative tests are the same processing conditions used for production of commercial prior art materials and thus represent the current optimum processing conditions taking all factors into account.

Materials made according to the method of the present invention may also receive post-sintering thermal treatments such as cryogenic treatment at  $-120^{\circ}\text{C}$  or below to convert any residual austenite phase to martensite, followed by tempering to make the martensite softer, more dimensionally stable and make it amenable to machining.

Thus, according to a feature of one embodiment of the present invention, the powder mixture contains a powder component comprising a relatively un-alloyed iron powder and a powder component comprising a steel powder containing at least some chromium or other martensite promoting element as an alloying element in addition to the pre-alloyed or diffusion bonded iron-copper powder. Alternatively or additionally the powder mixture may contain addition(s) of elemental martensite promoting material such as molybdenum and/or nickel for example.

Examples utilising M3/2 high speed steel powders are described herein, however, any other suitable tool steel or high speed steel, for example, chromium-containing steel powder may be employed depending upon the application in which the article produced therefrom is to be used.

An example of an alternative steel material is so-called 316 steel which is a stainless steel comprising in weight%: 17 Cr/ 2 Mo/ 13 Ni/ Bal Fe and which is substantially carbon free.

Thus, it appears that the manner in which copper is introduced into the sintered ferrous material, i.e. by being associated with the iron where there has been prior treatment causing reaction therebetween, has an unexpected and synergistic effect in aiding diffusion of chromium or other martensite promoting elements through the iron matrix to assist in the transformation to martensite on cooling after sintering or by transformation of retained austenite by cryogenic treatment.

The composition of the iron-copper pre-alloyed or diffusion-bonded material may be any desired, e.g. iron-20 copper. Powder mixtures may be made up having powder components comprising: iron; iron-copper; pre-alloyed steel powder; and, carbon powder, for example. The amount of iron-copper pre-alloy powder will depend upon the final required copper content in the article and on the initial composition of the iron-copper pre-alloy powder.

The use of iron-copper pre-alloyed and/or diffusion bonded material in a powder mixture together with an

addition on elemental copper powder is not precluded and in some circumstances may be beneficial. The use of both pre-alloyed and diffusion bonded iron-copper powder may also be employed in a powder mixture.

5

The pre-alloyed iron-copper material appears to be somewhat more effective in promoting the formation of martensite in iron grains than does diffusion bonded iron-copper material. Therefore, the use of the pre-alloyed material is preferred, however, it is pointed out that the diffusion bonded material produces martensite after sintering and subsequent processing whereas prior art infiltrated materials do not produce any martensite in the iron grain cores, the cores comprising only mixtures of pearlite and ferrite.

15

According to a second aspect of the present invention, there is provided a sintered article produced by the first aspect of the present invention.

20

In order that the present invention may be more fully understood, examples will now be described by way of illustration only with reference to the accompanying drawings, of which:

25

Figure 1 shows a histogram showing wear of valve seat inserts in an engine test on material made according to the present invention; and

30 Figure 2 which shows a graph of tool wear vs number of parts machined for materials made according to the present invention and prior art material.

Valve Seat Insert Material- Example 1

5 Ferrous powder mixtures of a typical composition used in the production of valve seat inserts for internal combustion engines were prepared by various routes. The compositions of the powder mixtures in terms of the actual constituent component powders used to make them were as set out below in Table 1:

10

Table 1

Constituent wt %	M 3/2	Graphite	MoS <sub>2</sub>	Elemental Cu	Fe-Cu powder	Lub Wax	Fe Powder
Example 1	45	0.55	1	6	47.47	0.75	-
Example 1a	42.9	0.42	0.87	13	-	0.75	42.9
Example 1b	49.75	0.5	-	Infiltrated	-	0.75	49.75

15 Example 1 was a material prepared by the method of the present invention where all of the iron and a proportion of the copper were added as pre-alloyed iron-20 copper powder. The pre-alloy powder contributes about 9.5 weight% of copper to the final material. A further 6 weight% of elemental copper powder was added to the  
 20 initial powder mixture to bring the total copper up to 15 weight%. The steel pre-alloy powder was a water atomised M3/2 powder having a nominal composition of: 1 C; 4 Cr; 5 Mo; 3 V; 5 W. Since only 6 weight% of elemental copper powder was added, segregation was minimised.

25

Example 1a is powder mixture wherein all of the iron powder content is provided as pure iron powder and the copper content as 13 weight% of elemental copper powder. Whilst such material would not normally be made with such  
 30 a high content of elemental copper powder for the reasons discussed hereinbefore, the material was made to

determine the effect of the copper content on the diffusion characteristics of the chromium into the iron constituent.

- 5 Example 1b was made by the prior art process according to GB-A-2 188 062 wherein the copper is supplied via a simultaneous sintering and infiltration step.

10 All of the powders were blended according to established principles in a Y-cone mixer. Compaction pressure was in the range 650-800MPa in each case followed by sintering at around 1100°C in a conveyor furnace, all Examples being sintered under the same conditions. Following sintering all Examples were cryogenically treated at -  
15 120°C to transform any remaining austenite ( $\gamma$ -phase) in the structure and then tempered at 600°C for 2 hours to soften the martensite, make it more dimensionally stable and enhance machinability qualities.

- 20 Table 2 below gives the actual compositions in terms of the constituent elements, the density of the sintered material and its final hardness following cryogenic and tempering post-sintering treatment.

25 Table 2

Constituent wt %	C	Cr	Cu	Mo	S	V	W	Fe	Density Mgm <sup>-3</sup>	Hardness HRA
Example 1	1	1.8	15.5	2.9	0.4	1.4	2.3	Bal	7.2	64-67
Example 1a	0.9	1.7	13	2.7	0.3	1.3	2.1	Bal	7.0	59-64
Example 1b	0.9	2.0	15	2.5		1.5	2.5	Bal	7.95	67-71

The microstructure of samples made according to Example 1 showed a tempered martensite structure even in the cores of the iron grains. The martensite was formed on cooling  
30 from the sintering temperature. Cryogenic treatment was used to transform any retained austenite in the M3/2



phase of the material to martensite. The change from austenite to martensite is not easily seen under the microscope, the change being evidenced by increased hardness on the change from austenite to martensite.

5

Samples from Example 1a showed a microstructure comprising some martensite formed on cooling from the sintering temperature and retained austenite. Following cryogenic treatment, the retained austenite transformed to martensite in the M3/2 regions and the iron grains comprised mainly pearlite (a phase comprising a lamellar structure of ferrite and cementite) and some ferrite. The pearlite was formed by virtue of the carbon powder added as graphite, however, owing to the absence of chromium in the iron grain cores, no martensite was formed. On tempering, extensive decomposition of pearlite took place and the volume fraction of ferrite increased compared with that of the as-sintered state. Thus, the wear resistance of Example 1a material is inferior and the mechanical properties, as evidenced by the hardness figures, are also inferior.

Samples from Example 1b demonstrated almost identical structure and properties as did Example 1a. This material was made according to the known process of GB-A-2 188 062. The hardness of Example 1b was slightly higher than Example 1, this being attributed to the higher density of the material following infiltration. However, the material of Example 1b showed extensive quantities of inherently weaker ferrite areas after tempering and not the desirable tempered martensite structure shown by Example 1 made according to the process of the present invention.

Figure 1 shows a histogram of valve seat insert wear of valve seat inserts, made from the material of Example 1, in the exhaust positions of a 1.8l, 4-cylinder, 16-valve engine which was run for 180 hours at 6000 rev/min on unleaded gasoline, the engine having Stellite (trade name) faced valves. The success criteria for this test is that valve seat insert wear must not exceed 100 $\mu$ m. As may be seen from Fig.1 the maximum wear was at valve seat position 4 at 60 $\mu$ m, all other inserts having wear of about 30 $\mu$ m or less.

Thus, it is clear from Examples 1, 1a and 1b that the only substantive difference in the manufacture thereof was the manner in which the copper was introduced into the sintered material. It is believed that the improved structure and properties are directly attributable to the use of the iron-copper pre-alloyed materials wherein at least a proportion of the copper is indivisibly associated with the iron and stem from the enhanced diffusion promoted by this pre-alloyed material.

#### Example 2

A powder mixture comprising 45 wt% M3/2 tool steel powder/ 0.55C/ 1 MoS<sub>2</sub> / 6 Cu/ 47.45 FeCu20 (diffusion bonded powder)/ 0.75 lubricating wax was made. This mixture was compacted into green compacts at 770MPa to a green density 7.1 Mgm<sup>-3</sup> and sintered at about 1100°C under a continuous flowing nitrogen-hydrogen gas atmosphere in a conveyor furnace. The sintered articles were cryogenically treated at -120°C or below to convert retained austenite to martensite and finally tempered at 600°C. Density of the sintered material was 7.0 Mgm<sup>-3</sup>. The

hardness of the as sintered material was 61HRA; that of the cryogenically treated material 65HRA; and that of the cryogenically treated and tempered material 62-65 HRA.

- 5 The microstructure of the Example 2 material (made with diffusion-bonded iron-copper powder) after tempering, (following sintering and cryogenic treatment) showed some small occasional areas of ferrite in the iron-rich non-tool steel phase. However, this iron-rich phase comprised  
10 essentially pearlite rather than the extensive regions of ferrite typified by the prior art material made using the infiltration technique.

15 Example 3

A mixture comprising in weight%: 75% pre-alloyed Fe-Cu20 powder/ 23% 316 stainless steel powder/ 0.75% MoS<sub>2</sub> powder/ 1% carbon powder was prepared; this material  
20 being coded N1. The composition of the 316 stainless steel was 17 Cr/ 2 Mo/ 13 Ni/ bal Fe. A comparative example coded N was made from the following mixture in weight%: 70.9% unalloyed iron powder/ 27% 316 stainless steel powder/ 0.9% MoS<sub>2</sub> powder/ 1.2% carbon powder. Both  
25 materials were compacted at 770MPa. However, material N1 was sintered only (as there was about 15 wt% Cu provided by the Fe-Cu pre-alloy) and material N was simultaneously sintered and infiltrated according to the known prior art process. The final theoretical overall composition of  
30 both materials N1 and N in weight% was: 1 C/3.9 Cr/15 Cu/0.9 Mo/3 Ni/S 0.3/bal Fe. The sintering/infiltration steps were carried out at about 1100°C under a flowing nitrogen/hydrogen atmosphere. Both materials following sintering were cryogenically treated and tempered.

The N1 material showed a microstructure having no ferrite, even in the cores of the grains which were predominantly iron. The structure of this material showed essentially a tempered martensite structure. The N material on the other hand showed extensive ferrite in the iron grains with a pearlitic structure in the transition zones between prior iron particles and 316 stainless steel particles even though this material had slightly higher carbon at 1.2%. Thus, again the influence of the copper being indivisibly associated with the iron is shown in the resulting structure after processing.

#### Example 4

15

Further mixtures denoted as material FMCA and FMCD were made according to the present invention. The blend compositions of these materials in terms of the constituents in the powder mixtures are given below in Table 3.

20

Table 3

	FMCA	FMCD
Fe-20 Cu (pre-alloyed)	75	75
C	1.35	1.35
Mo	0.5	
MoS <sub>2</sub>		1
Unalloyed Fe	23.15	22.65
Lubricating wax	0.75	0.75

25

The materials were compacted at 770 MPa and sintered at about 1100°C under a continuous gaseous atmosphere as with previous examples. The resulting densities and hardnesses of the sintered materials are given below in

Table 4. For these samples no post-sintering heat treatment was carried out.

Table 4

5

	FMCA	FMCD
Green density, $\text{Mgm}^{-3}$	7.05	7.05
Sintered density, $\text{Mgm}^{-3}$	7.35 - 7.40	7.15 - 7.20
Hardness, HRB	99 - 101	95 - 98

In the FMCA material made according to the present invention pre-alloyed Fe-Cu powder and 0.5% elemental Mo powder were used in the initial powder mixture. The FMCA material showed extensive Mo-rich zones and martensitic and bainitic areas associated with these zones. The FMCA material also showed grain boundary carbides. The microstructure of the FMCA material was somewhat similar to a comparative material, coded FMC (unalloyed iron powder, 1.35% C, 0.5% Mo), wherein the copper content was provided by a simultaneous sintering and infiltration process according to the prior art. Apart from the infiltration step, the sintering conditions were the same as those for the FMCA and FMCD materials. In the FMC material grain boundary carbide was present, the matrix was pearlite and the Mo-rich zones associated with the Mo particles were present but very small compared with the FMCA material.

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During sintering, the  $\text{MoS}_2$  in the FMCD material undergoes partial decomposition and donates free Mo to the structure which potentially is able to generate a localised martensitic/bainitic structure associated with the Mo-rich zones. Some of the sulphur from decomposed  $\text{MoS}_2$  reacts with iron and copper to form metallic sulphides which are beneficial for improving

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machinability. In the FMCD material no carbide networks could be seen and the matrix was pearlitic.

Figure 2 shows a graph of tool wear vs number of parts  
5 machined for FMC, FMCA and FMCD materials. The Figure  
confirms that the materials using pre-alloyed Fe-Cu  
powders which give rise to extensive martensitic/bainitic  
areas do not have their machinability impaired in spite  
of the stronger, more wear resistant material structures  
10 so formed. Indeed, the machinability of the both the FMCA  
and FMCD materials is superior to the FMC material made  
by a prior art process.

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## CLAIMS

1. A process for the manufacture of a ferrous-based sintered article containing copper in the range from 12 to 26 weight%, the process including the steps of: making a powder mixture having a desired composition, at least a proportion of a total content of iron and copper being provided by an iron powder having copper indivisibly associated therewith; compacting said powder mixture to form a green compact of an article to be produced and sintering said green compact.
2. A process according to claim 1 wherein the copper content lies in the range from 15 to 20 weight%.
3. A process according either claim 1 or claim 2 wherein the powder mixture contains a steel powder.
4. A process according to claim 3 wherein the steel powder contains chromium.
5. A process according to claim 3 wherein the steel powder contains molybdenum.
6. A process according to claim 3 wherein the steel powder contains nickel.
7. A process according to claim 3 wherein the steel powder is a high-speed steel powder.
8. A process according to claim 7 wherein the steel powder is an M3/2 steel powder.
9. A process according to claim 3 wherein the steel powder is a stainless steel powder.
10. A process according to claim 9 wherein the stainless steel powder is 316 steel.
11. A process according to any one preceding claim wherein the powder mixture contains carbon powder.
12. A process according to any one preceding claim wherein the iron-copper material is selected from

the group comprising: a diffusion bonded iron-copper powder and pre-alloyed iron-copper powder.

13. A process according claim 12 wherein the iron-copper material has a composition in weight% of Fe-20 Cu.
- 5 14. A process according to any one preceding claim wherein the powder mixture also includes elemental copper powder.
15. A process according to any one preceding claim wherein the powder mixture includes an element which promotes the formation of martensite.
- 10 16. A process according to claim 15 wherein the element is selected from the group comprising: chromium, molybdenum and nickel.
- 15 17. A process according to any one preceding claim further including the step of cryogenically treating the sintered material.
18. A process according to any one preceding claim further including the step of tempering the sintered material.
- 20 19. A process according to any one preceding claim further including the step of providing molybdenum disulphide or tungsten disulphide in the powder mixture.
- 25 20. A sintered ferrous-based material article when made by the process of any one of preceding claims 1 to 19.
21. A sintered article according to claim 20, the article comprising a valve seat insert for an internal combustion engine.



Fig. 1

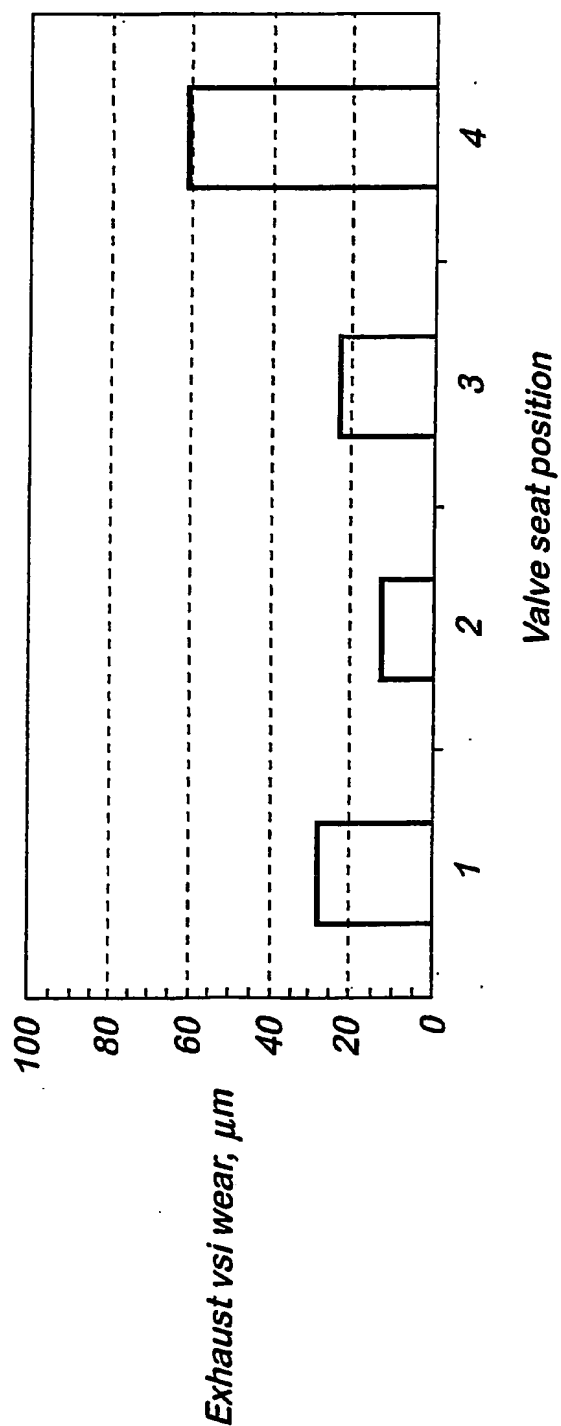
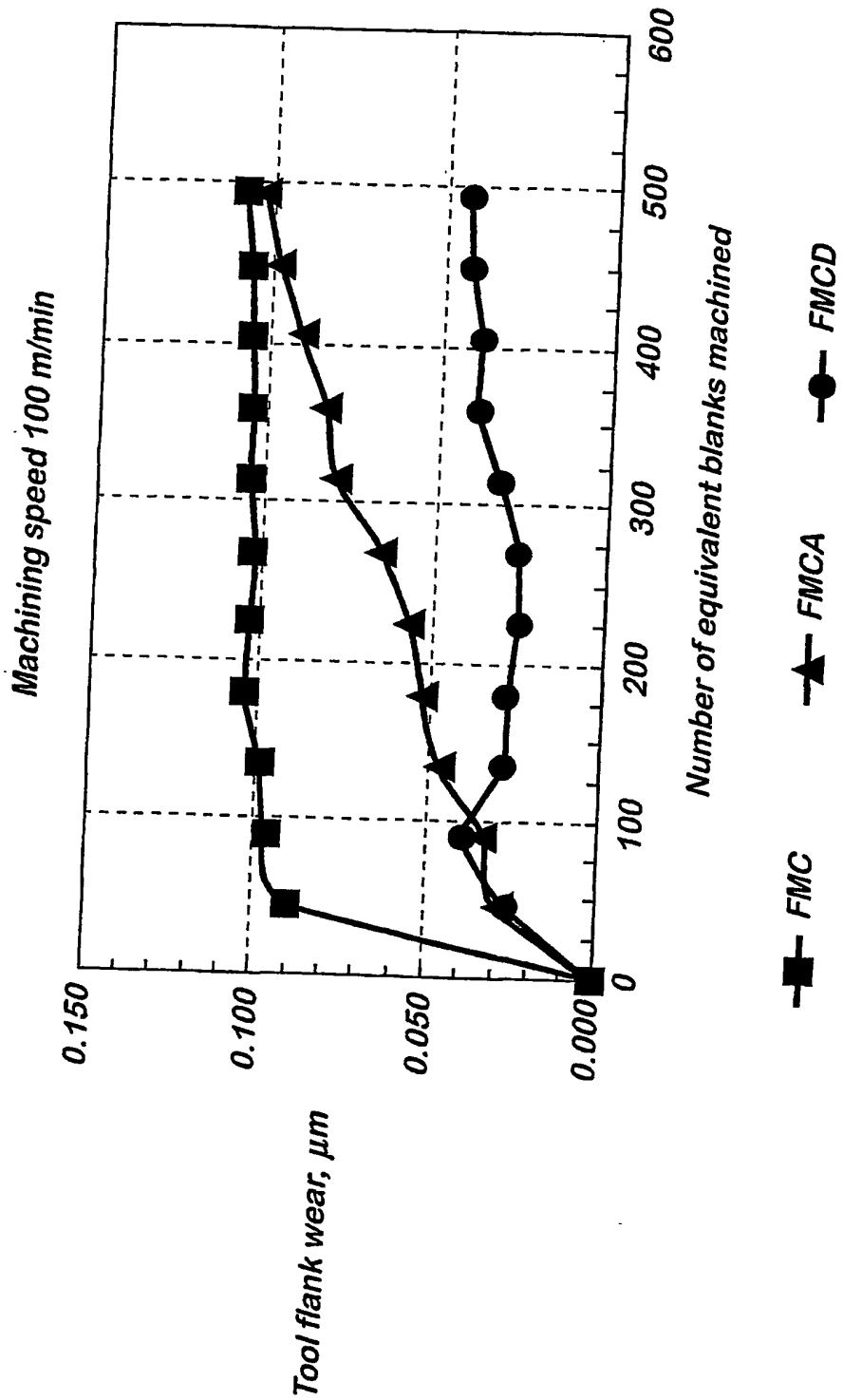


Fig. 2



## INTERNATIONAL SEARCH REPORT

PCT/GB 02/00176

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C22C33/02

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, COMPENDEX

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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X	US 3 694 173 A (FARMER EDWIN B ET AL) 26 September 1972 (1972-09-26) the whole document ---	1-21
X	US 3 752 712 A (HOLCOMB R) 14 August 1973 (1973-08-14) abstract column 2, line 18 - line 50 ---	1,20
X	CH 275 201 A (PLANSEE METALLWERK) 15 May 1951 (1951-05-15) page 1, line 18 - line 48; examples --- -/--	1,20

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

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- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

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- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \* & \* document member of the same patent family

Date of the actual completion of the international search

21 March 2002

Date of mailing of the international search report

09/04/2002

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## INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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